WHOI-94-06

Woods Hole
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Technical Report

Funding was provided by the National Science Foundation under Grants OCE 85113910, OCE 8515695, OCE 8711032 and OCE 9101466.

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Approved for Distribution:

Geoffrey Thompson

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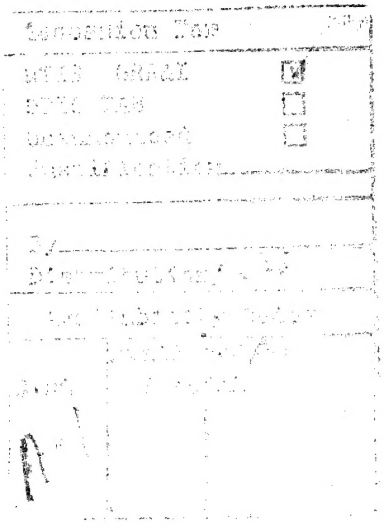

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ABSTRACT

A method is described to measure rare-earth elements (REE) in natural water samples. An iron hydroxide precipitation followed by ion-exchange chromatography is used to concentrate and separate the REE from other matrix components. Additionally, the rare-earth elements themselves are separated into three fractions using an organic acid with a second cation column. Instrumental detection is by isotope dilution mass spectrometry (IDMS) using either thermal ionization mass spectrometry (TIMS) or inductively coupled plasma-mass spectrometry (ICP-MS). Excellent precision is shown by many duplicate and replicate analyses. Blanks are 1-2% or less of samples.

INTRODUCTION

The composition of rare earth elements (REE) provides geochemists with a valuable tool for understanding many basic processes operating in both solid earth and in aqueous systems such as rivers, estuaries and oceans. Such processes include the differentiation and chemical evolution of the earth, chemical weathering on the continents and oceanic cycling. Key books and papers on these subjects include the following: Henderson (1984), Taylor and McLennan (1985), Faure (1986), Elderfield (1988), Goldstein and Jacobsen (1988), Elderfield et al. (1990), Piepgras and Jacobsen (1992) and Sholkovitz (1993).

Because the concentrations of REE in natural waters are low (1-500 pmol/Kg) and variations are small, a sensitive and high precision method of analysis is required. This report describes a method used at Woods Hole Oceanographic Institution (WHOI) in Dr. Edward Sholkovitz's laboratory. It is an adaptation of a method used in Dr. Stein Jacobsen's laboratory at Harvard University (Piepgras and Jacobsen, 1988, 1992). Low concentrations require a preconcentration step followed by the separation of REE and ultimately their mass spectrometric analysis. After pre-concentrating the REE, samples are processed, first through a cation exchange column using mineral acids, to separate REE from most major and trace elements (Crock, et al, 1986; Greaves, et al, 1989). A second ion exchange column using an organic acid serves to separate the REE themselves into three fractions: light (LREE), middle (MREE) and heavy (HREE). Although three filaments per sample must be analyzed, this separation greatly simplifies mass spectrometry since intra-element interferences are virtually eliminated. As a result, the analytical error is minimized (Piepgras and Jacobsen, 1992; Sholkovitz et al, 1992). High precision is achieved by using the method of Isotope Dilution Mass Spectrometry (IDMS) after Thirwall (1982) and Greaves et al (1989). Our method differs from that of Greaves et al. (1989) in that they collect and carry out the mass spectrometry of REE as a single group. This entails many corrections for isobaric interferences. While this method has produced high quality data (e.g., Elderfield, 1988; Bertram and Elderfield, 1993), we prefer to apply a second column separation which eliminates most of the interferences. This method is also preferred by Jacobsen's laboratory (Piepgras and Jacobsen, 1992).

METHODS

I. PLASTICWARE AND CHEMICALS

A. ***Plasticware*** - Both Teflon PFA and low density polyethylene (LDPE) bottles and vials are used in the analytical procedure. Initial cleaning of Teflonware consists of soaking in detergent followed by Milli-Q rinses and a two-day soak in 8M HNO_3 (reagent grade). Thereafter,

recycled Teflon vials are soaked in detergent, heated overnight in 4M HNO_3 (reagent grade), then rinsed with clean water. Sample collection bottles (LDPE) are filled with 1M HCl (reagent grade) and heated in a 60°F oven for two days. Final rinses are with Ba-Free H_2O (described below).

B. ***Water*** - The standard water used in this procedure is produced by a Milli-Q Type I reagent grade water system (Millipore Corp.) to a resistivity of 18 megohm-cm. The four bowl unit consists of: prefilter, activated carbon and two mixed-bed ion-exchange cartridges. Final filtration is done with a 0.2 micron Milli-Pak filter cartridge. In addition, the Milli-Q water is further purified by passing it through a 25 mL Teflon column filled with Bio-Rad AG 50WX8, 50-100 mesh resin which has been cleaned with 4M nitric and hydrochloric acids produced from two-bottle stills. This resulting water is called "Ba-Free Milli-Q" because this final column's purpose is to remove ubiquitous barium from the water. Barium and its oxides, fluorides and chlorides are the primary interferences to REE during mass spectrometry.

C. ***Acids*** - "Clean" nitric and hydrochloric acids are produced from commercial, reagent grade acids using two-bottle stills. A still consists of two 1 liter Teflon FEP bottles (Nalgene) connected at a 90° angle via a drilled and threaded block of Teflon TFE. One bottle contains concentrated, reagent grade acid and is wrapped with a custom-made silicon rubber heating element (Hi-Heat Industries Inc.); the other bottle acts as the receiving vessel for the "clean" acid. A variable transformer is used to gently heat the generator bottle to a sub-boiling condition and purified, concentrated acid condenses in the receiving bottle. These acids are referred to as "clean" or "two-bottle" acids. The normality of the acids is determined gravimetrically by making accurate dilutions of the concentrated acids and measuring the specific gravity. Normality is then calculated using standard data from a chemical handbook. Acid dilutions used in the analytical procedure are made from this "clean" acid and Ba-Free Milli-Q.

D. ***Other Reagents*** - In addition to the mineral acids, the other chemicals used in the procedure have to be purchased in pure form or purified in the lab:

1. Ammonium Hydroxide - used to co-precipitate the REE with iron hydroxide. Approximately 600 mL of reagent grade NH_4OH is placed in the generator bottle of a two-bottle still and 100 mL of Ba-Free water is placed in the receiving bottle. No heat is applied. The still is left to equilibrate for three days. The "clean" solution is poured off into a storage bottle and the procedure is repeated until 500 mL of clean NH_4OH is produced.

2. Iron Carrier - used to co-precipitate the REE. A 2 mg/mL stock solution is made from pure iron (III) nitrate (Johnson Matthey; Puratronic; 99.999%). One mL of this solution is added to each liter of seawater to be analyzed.

3. Enriched REE Isotope Spike - the spike used in our analyses was obtained from Dr. Harry Elderfield. The REE concentrations and isotopic ratios of the spike are given in **Table 1** and Greaves et al. (1989).

TABLE 1

Isotopic Composition of REE Spike

SPIKE ISOTOPE	MEASURED RATIO	SPIKE RATIO	NATURAL RATIO	NUMER. ABUND.
La-138	139/138	13.834000	1122.60000	0.99911
Ce-142	140/142	0.087489	7.99280	0.88480
Nd-145	146/145	0.133770	2.08200	0.17260
Sm-149	147/149	0.002332	1.08890	0.15070
Eu-153	151/153	0.005610	0.91461	0.47770
Gd-155	156/155	0.001270	1.38970	0.20470
Dy-161	163/161	0.005530	1.32260	0.24970
Er-167	166/167	0.031885	1.45640	0.33410
Yb-171	174/171	0.016440	2.22500	0.31840
Lu-176	175/176	0.403200	37.46200	0.97400

4. Methyllactic Acid (MLA) - used to separate the REE into three fractions. The MLA or 2-Hydroxylisobutyric acid [Aldrich Chemical Co.; 99%; $(CH_3)_2C(OH)CO_2H$] is prepared as a 0.4M solution with Ba-Free H_2O. Multiple 2 liter batches (83.30 g per 2 liters soln.) are prepared and filtered through 0.22 micron Durapore filter membranes (Millipore; GVWP 047 00) using polycarbonate filter housings (Sartorius; SM16511; 47 mm). These 0.4M stock solutions are then purified by passing them through the same type of column that is used to prepare Ba-Free H_2O (described above). Finally, three dilutions are made with Ba-Free Milli-Q:

i) 0.20M MLA; pH=4.30; 8 liters

ii) 0.20M MLA; pH=4.66; 4 liters

iii) 0.35M MLA; pH=4.77; 2 liters

pH adjustment is made with clean, "two-bottle" NH_4OH. The working dilutions are stored in acid-cleaned polyethylene carboys with spouts for easy dispensing.

E. ***Ion Exchange Resins*** - Resins are acid-cleaned by passing ten column volumes of first 4M HNO_3 and then 4M HCl through the resin column (reagent grade acids). A final Milli-Q water wash completes the process.

1. AG 50WX4, minus 400 mesh - used in the MLA separation of the REE. A batch of approximately 250 mL is acid-cleaned using a column assembled from Teflon components (Savillex Corp.; #502, 504, 501-25). The column is connected with Teflon tubing to a 4 liter carboy with spout. Several batches are cleaned in succession to provide a good supply of resin.

2. AG 50WX8, 100-200 mesh - used to separate REE from the starting matrix. This resin is not cleaned in a large batch but in the column just prior to adding the sample.

II. INITIAL SAMPLE TREATMENT

An aliquot of the sample (100-2,000 g for seawater) is weighed in an acid-cleaned, tared polyethylene bottle and an appropriate amount (about 0.1 g per Kg of seawater) of the isotope-enriched spike containing La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Lu is added. The spike is added to a precision of 0.0001 g by weighing a spike-containing vial before and after taking out an aliquot and transferring it to a sample bottle. The sample, which was acidified upon collection to a pH of 2, is equilibrated for at least three days, but typically for a week. "Clean" iron carrier is then added and the REE are co-precipitated with $Fe(OH)_3$ by adding "clean" NH_4OH. The precipitation is done either in the original sample collection bottle or in another "clean" PE bottle, if an aliquot is taken for analysis. Small amounts of NH_4OH are added until the sample is pH=9. A pale yellow color is indicative of iron (III) hydroxide formation. The sample bottle is shaken well and left to equilibrate for 15-30 minutes after which pressure filtration is carried out using a polycarbonate filter housing (Sartorius, SM16511). The resulting precipitate, on a 0.22 μm Duropore membrane, is stored in a covered plastic filter holder prior to column chemistry (*see **Appendix A** for protocol*).

III. CLEAN-UP COLUMN

The $Fe(OH)_3$ precipitate is dissolved in 1.75M HCl, which is added directly to the plastic filter holder. This yellow solution is then passed through ion exchange resin in a small quartz column, followed by washes of 1M nitric acid. This column separates major and trace elements from the REE group (Greaves, et al, 1989). The REE are retained on the column while other elements (primarily Fe and Ba) are eluted in the wash fractions. Finally, the REE are eluted into 5 mL conical-bottomed teflon beakers (Savillex Corp.) with 4M nitric acid. The sample solutions are evaporated to dryness in an enclosed evaporator box under filtered air. The evaporator box is an acrylic desiccator cabinet (Plas-Labs) equipped with a specially designed hot plate. The hot plate is constructed of a 200 watt silicon rubber heater (Hi-Heat Industries Inc.) sandwiched between two teflon-coated aluminum plates. Two small diaphragm air pumps (Delta Power Corp.; PV-1100) are used to pump filtered (0.2 micron) air through the evaporator box during sample evaporation. The air flow speeds up the rate of evaporation.

IV. REE SEPARATION

In order to simplify mass spectrometry measurements, the REE are separated into three groups, light (LREE), middle (MREE), and heavy (HREE), on a methyllactic acid (MLA) column. The column is pressurized and fractions are collected using a drop counting technique (*see **Appendix B***). Filtered nitrogen gas is used for pressurization through an in-line secondary regulator set at 6 psi. The custom-made capillary quartz column has a flow rate of about one drop per minute. The entire separation requires 280 drops (~ 14 mL) and takes approximately six hours to complete. Each column is calibrated at least three times to make certain that the elution pattern is reproducible. The calibration procedure (Shirey, et al, 1987) is carried out each time new batches of resin and chemicals are prepared and is done outside the cleanroom where samples are processed. Each column is thoroughly acid-cleaned and rinsed before being returned to the cleanroom and put in service.

The residue from the first column is dissolved in 0.75M HCl and is loaded on a MLA column which had been prepared and generated the previous day with 0.20M MLA (pH=4.30). HREE (Dy, Er, Yb, Lu) elute first in approximately 2 mL of 0.20M (pH=4.30) MLA and are collected in 7 mL, round-bottom Teflon vials (Savillex Corp., #02.25R). Excess 0.20M MLA (pH=4.30) is removed from the column reservoir and approximately 7.5 mL of 0.20M MLA (pH=4.67) is added to elute the MREE (Nd, Sm, Eu, Gd). A third change of acid, approximately 5 mL of 0.35M MLA (pH=4.77), brings off the LREE (La, Ce).

The three REE fractions are evaporated to dryness at approximately 100°C. The remaining MLA residue is destroyed with aqua regia made from clean acids. After this acid treatment, usually 100 µL each of concentrated HCl and HNO_3, the residue has been reduced to a small black dot. The sample vials are then stored, awaiting mass spectrometry.

V. MASS SPECTROMETRY

A. *Filament Preparation*

Samples are loaded on VG type filament support beads (Cathodeon, Ltd., Cambridge, England; #519-single; #517-triple). Single Ta filaments are used for LREE and MREE (H. Cross Co., high-purity Ta, thickness=0.001", width=0.020"). HREE are run on Ta-Re-Ta triple filaments (Rembar Co., Inc., Dobbs Ferry, NY; zone-refined Re; thickness=0.0012"; width=0.030"). All filaments are heated to remove contaminants in a degassing chamber, previously pumped down to a vacuum of 10^{-7} torr with a diffusion pump.

Single Ta filaments are degassed at 2.5 amps for 1 hour. Triple filaments are degassed as follows: center Re at 5.0 amps for a half hour; then Ta sides at 2.5 amps for 1 hour while

maintaining Re center at 1 amp. Sequential rather than simultaneous degassing of center and side filaments prevents cracking of glass bead supports for the triple filaments.

Triple filament preparation is accomplished by bending the side support posts back to ~30° angle from the vertical. Welding of the wire ribbon, degassing, sample loading and conditioning are all done in this configuration. The side posts are very carefully bent back to the vertical prior to installation in the MS.

B. *Sample Loading*

The filament loading apparatus is a set of electrical contacts mounted in a block of polyethylene and wired to a DC power supply. The stainless steel posts of the filament bead are inserted into the electrical contacts. The electrical block is set on the stage of a binocular microscope so sample evaporation can be closely observed.

The evaporated sample residue from the MLA column is taken up in 1-2 μL of high-purity 0.2M HNO_3 using a micropipette (Drummond, Model #203) with disposable polyethylene capillary tubing. A drop (<1 μL) is transferred to the center of the filament and evaporated at a current of 1 amp. With the current maintained at 1 amp, the remainder of the sample is spotted on the filament in several aliquots and is evaporated to dryness. When the sample is on the filament in the form of a residue, the current is slowly increased from 1 to 2 amps or until the center of the filament just barely begins to glow. As the current is increased, the residue chars and turns black. Experience has shown that the appearance of the residue, which can vary in texture and color, has little to do with the successful production and measurement of a MS signal. The REE apparently are not bound up with the residue but with the filament metal before the residue forms. Even in instances where the residue has flaked off, strong REE signals are produced.

After sample loading, the filaments are returned to the degassing bench and "conditioned" under a vacuum of 10^{-7} torr by heating to a dull orange for 5 min. This step drives off gases from the loading process. The sample filaments are now ready for installation in the mass spectrometer.

C. *Isotope Dilution Mass Spectrometry*

1. Technique Used At WHOI

Measurement of REE concentrations by IDMS are made on a VG 354 Thermal Ionization Mass Spectrometer (TIMS) of the Isotope Geochemistry Facility in Dr. Mark Kurz's laboratory. Focusing is done under manual control using the SCAN program. The filament current is slowly ramped up by the operator until a peak of several hundred millivolts is observed. The SCAN program is then paused at the peak center and the focus is optimized. After exiting SCAN, the MANUAL program is invoked to achieve optimum peak centering, and for data collection using the general peak jumping routine of the VG software. The various peak jumping types used are

shown in ***Appendix C***. REE signals in the range 10 mV - 1 V are measured on a Daly detector at a vacuum of 10^{-8} torr. An integration time of 5 sec. is used at each mass and data are taken in a single block of 20 mass scans. No correction is made for mass fractionation. The isotopic composition of the spike is given in **Table 1**.

The REE content of Sargasso Sea surface water is shown in **Table 2**. As an upper limit, filament loads range from 2.3 ng for Nd to 0.10 ng for Lu in a typical one liter sample. Since the REE have been chemically purified and separated, three beads are analyzed per sample. The mass spectra are generally free from interferences; the only potential interferences come from fluorides, chlorides, and oxides of barium.

TABLE 2
Typical REE Concentration of Sargasso Seawater

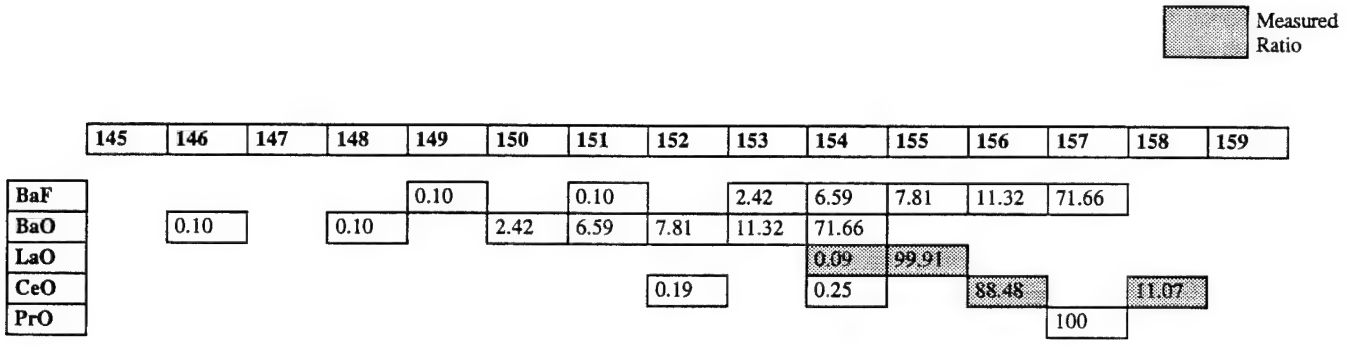
	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
pmol/Kg	16.00	15.70	15.90	3.51	0.92	5.33	5.84	4.74	4.04	0.55
ng/Kg	2.20	2.20	2.30	0.53	0.14	0.84	0.95	0.79	0.70	0.10

The LREE begin to ionize as oxides from Ta single filaments at approximately 1200°C, with stable beams measured in the range 1250-1350°C. The CeO ratio 156/158 is measured first. The filament current is then slowly ramped up to give a significant ^{154}LaO peak, and the LaO ratio 155/154 is measured. Elemental barium is always present, but causes no interference to the LREE oxides. The presence or absence of barium oxides and fluorides is diagnosed by scanning the mass range 150-160 (see **Table 3**). A signal at mass 157 indicates either BaF or PrO. Although the MLA column elution scheme is set up to discriminate against Pr, variable amounts of Pr can be collected along with La and Ce. This means that a peak at mass 157 does not unequivocally identify BaF. Inspection of the mass range 150-153 has shown the presence of a 153 BaF peak in most samples. The absence of peaks at 150, 151 and 152 indicates BaO is not present. Generally the 153 peak is small in relation to the ^{154}LaO peak, but a correction for ^{153}BaF is applied to the ^{154}LaO peak based on the 153 peak. A correction to the ^{154}LaO peak is also made for the small CeO contribution at that mass. The ^{155}LaO and ^{156}CeO peaks are also corrected for BaF based on the 153 peak (see Table 3 and ***Appendix D***).

TABLE 3

LREE Natural Abundance

MASS NUMBER



The MREE (Nd, Sm, Eu and Gd) are also run on single Ta filaments. Eu emits at approximately 1200°-1275°C and ionizes relatively quickly. Sm and NdO signals are measured together between 1200-1350°C. Eu(151/153), Sm(147/149), and NdO(162/161) are all free of interferences. The fact that, on Ta ribbon, Sm emits as the metal and Nd as the oxide works to the analyst's advantage by eliminating intra-REE interferences. Finally, GdO(172/171) ionizes at approximately 1500°C. BaCl is a potential interference to GdO but at 1500°C, has already burned off. A signal at mass 175 is an indicator of BaCl (see **Table 4**).

The HREE (Dy, Er, Yb and Lu) all run as metals on triple (Ta-Re-Ta) filaments. The current on the center Re filament is slowly raised to approximately 4.6-4.8 amps (2,000°C). Yb(174/171) is measured first at a side filament current of approximately 1.5-1.7 amps . Next, Dy(163/161) and Er(166/167) are measured together at approximately 1.8-2.0 amps. Finally, Lu(175/176) is detected at approximately 2.0-2.2 amps. The ratio 171/176 is also monitored for Yb, which interferes with Lu. Data for Lu is collected only when Yb is gone or minimal (see **Table 5**).

2. Technique Used at Harvard University

a). TIMS

Some measurements were made in Dr. Stein Jacobsen's laboratory at Harvard on a Finnigan Thermoquad (THQ). The THQ is a Thermal Ionization Mass Spectrometer instrument utilizing a quadrapole unit for mass separation and focusing. As with the VG magnetic sector instrument at WHOI, the LREE are detected as oxides on Ta single filaments. The MREE, however, are run on double Re filaments with Nd, Sm and Eu emitting as metals and Gd as an oxide. The HREE are also run as metals on double Re filaments. Filaments are degassed at approximately 4.0 amps for 30 minutes, but the sample loading procedure is essentially the same as that used at WHOI. Mass data is collected in 3 blocks of 20 scans each with an integration time of 1 sec. per peak.

TABLE 4

MREE Natural Abundance

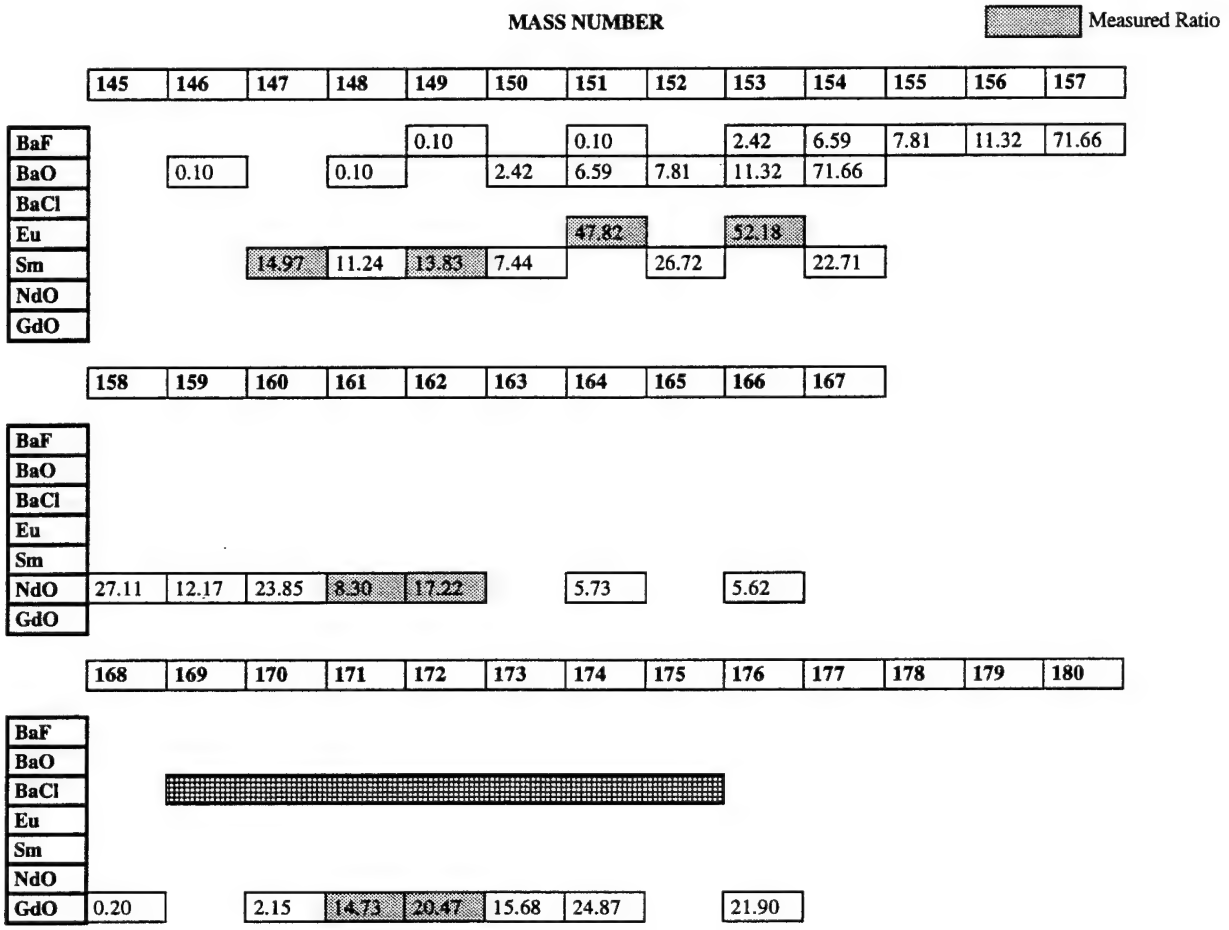
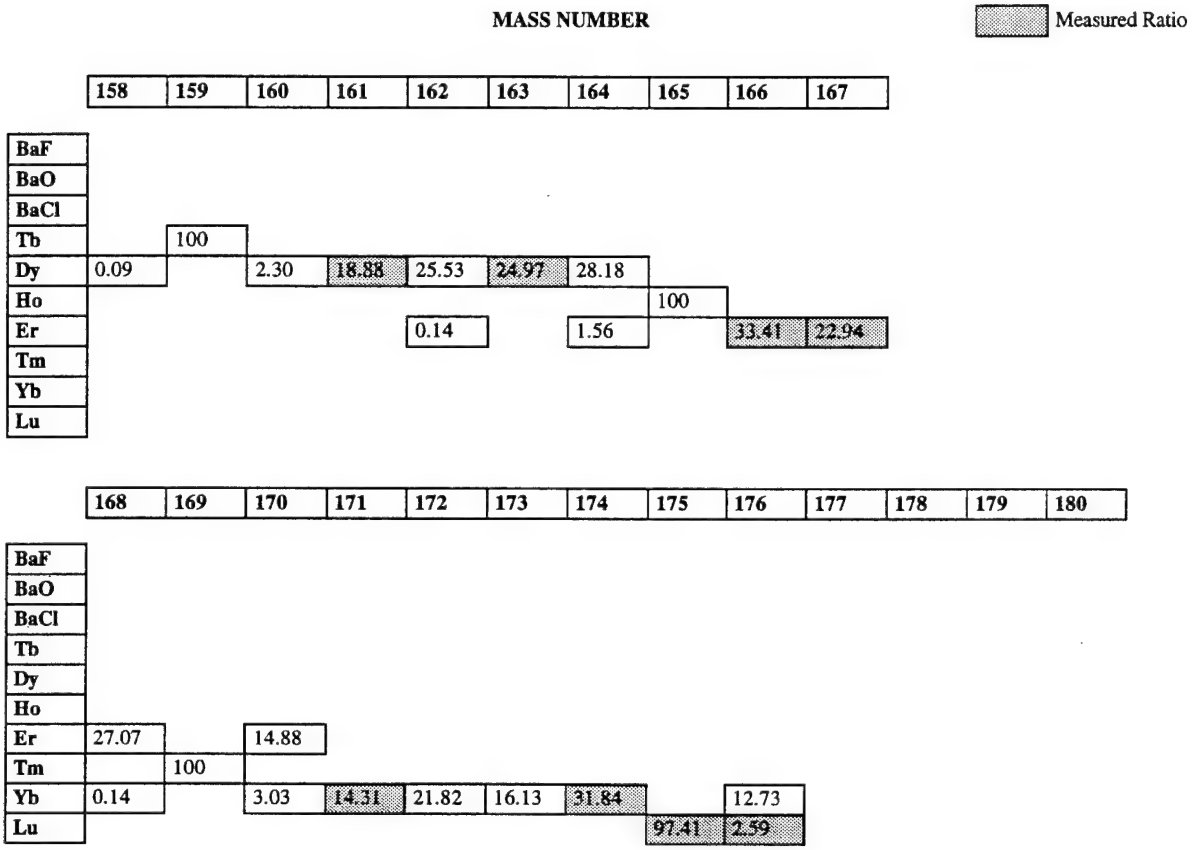


TABLE 5
HREE Natural Abundance



b). Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

Sholkovitz's laboratory has measured REE concentrations in river waters by ICP-MS. The higher concentrations of fresh waters make ICP-MS a viable alternative to thermal ionization. At the present state of technology, ICP-MS doesn't have the sensitivity required by this laboratory to make precise measurements of REE at the low levels found in seawater. Although Moller et al. (1992) report an ICP-MS method for sea water, the precision ranges from 4 to 12%. To decipher variations within the oceans, precisions of 1% are a great advantage (Sholkovitz and Schneider, 1991; Piepgras and Jacobsen, 1992).

We used a VG PlasmaQuad PQ2+ at Harvard University. The standard operating conditions of the instrument are as presented in Table 6. Samples were run following either the single column separation of the REE into one group or after the three stage separation into LREE, MREE and HREE fractions. The latter is preferred. The sample media consisted of 4 mL of 1M HCl.

TABLE 6

VG PlasmaQuad PQ2+ ICP-MS

INSTRUMENT OPERATING CONDITIONS

Plasma Gases	all argon
Forward Power	1.35 KW
Reflected Power	< 5 W
Nebuliser gas flow rate	0.74 l/min
Coolant gas flow rate	13 l/min
Auxiliary gas flow rate	0.5 l/min
Sample Uptake rate	0.8 mL/min (pumped)
Nebuliser	Meinhard concentric - recessed tip
Spray Chamber	water cooled (5 C.)
Ion Lenses	optimized on In and Ho
Scan Range	134 - 180 amu
Skipped regions	none

Isotope dilution technique was used and the measured ratios are the same as those used in TIMS (Tables 3-5). Account must be taken of isobaric interferences however, and in general, the most abundant isotope, free from isobaric overlap, is chosen for the determination of each element. For some of the REE the interferences are trivial but for La, Ce, Gd and Lu, corrections must be made.

Corrections For Isobaric Interferences

1. Barium

The ^{138}Ba isotope interferes with the ^{138}La signal. Barium ionizes very easily and presents a challenge with respect to determining La. In many samples there is so much Ba interference that an accurate La measurement cannot be made. This is particularly the case when only a single column is employed and all the REE are in the same sample. As the 138 signal consists of both Ba and La, the measured 139/138 ratio equals $^{139}La/(^{138}La + \mathit{^{138}Ba})$. The Ba 138 portion of the denominator (in *italic* print) can be determined by measuring ^{137}Ba and using the natural ratio of $^{138}Ba/^{137}Ba$. In a similar manner, a second independent correction can be made by

measuring ^{135}Ba and using the natural $^{138}Ba/^{135}Ba$ ratio. The following equations show the how the interfering ^{138}Ba counts are determined.

$^{138}Ba = {}^{137}Ba\ (^{138}Ba/^{137}Ba)_{nr} = {}^{137}Ba\ (6.3304)$ where nr = natural ratio.

$^{138}Ba = {}^{135}Ba\ (^{138}Ba/^{135}Ba)_{nr} = {}^{135}Ba\ (10.8741)$.

The $^{139}La/^{138}La$ ratio, now corrected for ^{138}Ba is then calculated.

2. $^{140}Ce / ^{142}Ce$

A interference correction for the ^{142}Nd isotope on the ^{142}Ce signal is required. This is accomplished by measuring ^{143}Nd and applying the natural ratio of $^{142}Nd/^{143}Nd$ which equals 2.2276. Hence,

$$(^{140}Ce / {}^{142}Ce)_{corrected} = {}^{140}Ce_{measured}/(^{143}Nd_{measured} * 2.2276)$$

3. $^{156}Gd/^{155}Gd$

Oxides of ^{139}La and ^{140}Ce, produced and quantified as $^{155}(LaO)$ and $^{156}(CeO)$, interfere with the measurement of $^{155}Gd/^{156}Gd$ ratios. The efficiency of oxide production varies from run to run depending on the operating conditions. It is best to run single element standard solutions of La and Ce (along with samples) to directly determine the production of LaO and CeO. After measuring many standards over a period of several months, LaO is approximately 1.4% of the La counts and GdO is approximately 1.0% of the Ce counts. This leads to the following correction equation:

$$(^{156}Gd/^{155}Gd)_{corrected} = \frac{(^{156}Gd_{measured} - {}^{140}Ce_{measured} * 0.014)}{(^{155}Gd_{measured} - {}^{139}La_{measured} * 0.010)}$$

4. $^{175}Lu/^{176}Lu$

^{176}Yb adds to the measured ^{176}Lu counts. This isobaric interference is corrected for by measuring the ^{174}Yb counts and employing $^{176}Yb/^{174}$ Yb natural ratio which is 0.3998.

Therefore, the correction equation is as follows.

$$(^{175}Lu/^{176}Lu)_{corrected} = {}^{175}Lu_{measured}/(^{176}Lu_{measured} - {}^{174}Lu_{measured} * 0.3998)$$

Table 7 provides an example of the ICP-MS data and the differences between incorrected and corrected ratios.

TABLE 7

EXAMPLE OF ISOBARIC CORRECTIONS FOR ICP-MS:
CONNECTICUT RIVER WATER JANUARY 1992, #168, 0.22uM FILTERED

MASS	COUNT	UNCORRECTED 139 / 138		CORRECTED 139La / 138La
135	658	3.495	135Ba corr	49.9
137	1001		137Ba corr	108
138	7694			
139	26897			
		UNCORRECTED 140/142		CORRECTED 140Ce / 142Ce
140	35292	0.509		0.566
142	69310			
143	3098			
		UNCORRECTED 156 / 155		CORRECTED 156Gd / 155Gd
139	35292	0.168		0.142
140	26897			
155	12263			
156	2067			
		UNCORRECTED 175 / 176		CORRECTED 175Lu / 176Lu
174	5752	0.903		1.76
175	4255			
176	4711			

RESULTS

I. CALCULATIONS

The concentrations of the individual REE are calculated using the basic IDMS equation:

$$C_{sa} = \frac{R_m - R_{sp}}{1 - \frac{R_m}{R_{sa}}} x \frac{W_{sp}}{W_{sa}} x \frac{C_{sp}}{A_n}$$

where:

C_{sa}	=	sample concentration
C_{sp}	=	spike concentration
R_m	=	measured ratio
R_{sa}	=	sample ratio
R_{sp}	=	spike ratio
W_{sa}	=	sample weight
W_{sp}	=	spike weight
A_n	=	ratio numerator abundance

All calculations are embedded in the appropriate spreadsheet column of a raw data table such as **Table 8**. The individual formulas for computing the concentration of each element are shown below in **Table 9**. The formulas are multiplied by 1000 in order to express concentration in pmol/Kg.

TABLE 8

Standard Raw Data Table for Calculating Concentrations

Concentrations = pmol/Kg

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1														
2														
3														
4	SAMPLE	Depth	Sam	Spk	La	La	Ce	Ce	Nd	Nd	Sm	Sm	Eu	Eu
5	ID	m	g	g	139/138		140/142		146/145		147/149		151/153	
6														
7	BATS30B													
8	05APR91 B1	1	1002.2	0.1003	55.28	14.50	0.682	13.65	0.3705	18.17	0.2045	5.53	0.2601	0.904
9	05APR91 B1R	1	887.6	0.1029	52.96	15.83	0.570	12.65	0.3351	17.53	0.1594	4.74	0.2396	0.934
10	05APR91 B2	20	985.1	0.1010	57.89	15.83	0.627	12.59	0.3609	17.76	0.1902	5.18	0.2602	0.927
11	05APR91 B3	40	986.7	0.1049	55.53	15.50	0.625	13.02	0.3492	17.34	0.1717	4.75	0.2555	0.937
12	05APR91 B5	80	1028.0	0.1033	57.06	15.21	0.619	12.15	0.3528	16.71	0.1689	4.40	0.2642	0.928
13	05APR91 B9	140	1009.7	0.1029	54.89	14.62	0.625	12.47	0.3487	16.59	0.1817	4.88	0.2559	0.900
14														
15					Gd	Gd	Dy	Dy	Er	Er	Yb	Yb	Lu	Lu
16					156/155		163/161		166\167		174/171		175/176	
17														
18	BATS30B													
19	05APR91 B1	1			0.3637	6.54	0.2389	5.67	0.3568	4.77	0.2991	3.93	1.5553	0.545
20	05APR91 B1R	1			0.3169	6.31	0.2189	5.90	0.3215	4.77	0.2744	4.10	1.4325	0.562
21	05APR91 B2	20			0.3630	6.69	0.2413	5.89	0.3512	4.78	0.3029	4.09	1.5709	0.566
22	05APR91 B3	40			0.3285	6.07	0.2351	5.91	0.3420	4.77	0.2925	4.06	1.5159	0.559
23	05APR91 B5	80			0.3373	5.94	0.2462	5.91	0.3553	4.76	0.3047	4.04	1.5985	0.569
24	05APR91 B9	140			0.3299	5.85	0.2387	5.77	0.3498	4.72	0.2998	4.01	1.5896	0.572

TABLE 9

Formulas for Calculating REE Concentrations

		Wsp/Wsa		Csp/An	Rm - Rsp		1 - (Rm / Rsa)		
La	=	D8 / C8	x	3.324	((E8 - 13.834)	/	(1 - (E8 / 1122.6)))	x	1000
Ce	=	D8 / C8	x	209.88	((G8 - 0.08749)	/	(1 - (G8 / 7.9928)))	x	1000
Nd	=	D8 / C8	x	630.36	((I8 - 0.13377)	/	(1 - (I8 / 2.0820)))	x	1000
Sm	=	D8 / C8	x	222.18	((K8 - 0.002332)	/	(1 - (K8 / 1.0889)))	x	1000
Eu	=	D8 / C8	x	25.403	((M8 - 0.00561)	/	(1 - (M8 / 0.9146)))	x	1000
Gd	=	D8 / C8	x	133.17	((E19 - 0.00127)	/	(1 - (E19 / 1.3897)))	x	1000
Dy	=	D8 / C8	x	199.05	((G19 - 0.00553)	/	(1 - (G19 / 1.3226)))	x	1000
Er	=	D8 / C8	x	110.72	((I19 - 0.03189)	/	(1 - (I19 / 1.4564)))	x	1000
Yb	=	D8 / C8	x	120.22	((K19 - 0.01644)	/	(1 - (K19 / 2.2250)))	x	1000
Lu	=	D8 / C8	x	4.5318	((M19 - 0.4032)	/	(1 - (M19 / 37.462)))	x	1000

II. REPLICATES

Many different samples have been analyzed in replicate to ascertain the reproducibility of the method. The replicate analyses are generally spaced over many months, and in some cases, several years. The column separations were carried out by four different people using different columns of the same type. Three different mass spectrometers were used. The overwhelming majority of measurements were made on the VG 354 at WHOI, but certain sample sets were analyzed using the VG PlasmaQuad ICP-MS and the Finnigan THQ at Harvard University.

Replicates done by ICP-MS and having the identifier 'SC' were only processed through a cation exchange column with HCl and HNO_3 eluants to separate REE from major matrix elements. In these cases, the REE were analyzed as one group. The identifier 'MLA' means the sample was passed through an additional column to separate the REE into light (LREE), middle (MREE) and heavy (HREE) fractions. Thus, each MLA sample required three individual mass spectrometric measurements.

A replicate set of Chesapeake Bay samples is shown in **Table 10**. The first three measurements (#40-42) were made at WHOI in early 1991. In July 1993, four more aliquots were analyzed, two at WHOI and two at Harvard on the THQ. The standard deviation for all elements on all seven measurements is 4% or less, with the exception of Ce at 8 %. One of the Ce data points (34.99) appears to be an obvious outlier. When it is excluded, the % Std Dev for Ce is 2.4.

TABLE 10
REPLICATES OF
CHESAPEAKE BAY WATER
0.22 μm FILTERED
REE in pmol/Kg

SAMP #	I.D.	METHOD	Ce ANOM	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
40	WHOI	TIMS-ID-MLA	0.28	49.90	28.40	46.40	10.53	2.78	17.00	17.10	15.20	15.20	2.40
41	WHOI	TIMS-ID-MLA	0.29	49.20	27.90	42.20	10.55	2.74	16.00	17.70	15.30	15.80	2.30
42	WHOI	TIMS-ID-MLA	0.29	49.10	28.70	43.60	10.52	2.76	16.30	17.40	15.00	15.70	2.40
450	WHOI	TIMS-ID-MLA	[0.35]	50.05	[34.99]	45.56	11.43	2.65	17.08	17.52	14.87	15.71	2.39
452	WHOI	TIMS-ID-MLA	0.29	49.99	29.23	45.81	11.48	2.71	16.96	17.57	14.95	15.75	2.46
451	HU - THQ	TIMS-ID-MLA	0.31	46.40	29.85	45.52	11.23	2.69	17.02	17.89	14.75	16.16	2.41
453	HU - THQ	TIMS-ID-MLA	0.31	45.21	29.04	45.54	11.23	2.69	17.11	17.74	14.79	16.01	2.42
		MEAN (7)	0.295	48.55	28.85	44.95	11.00	2.72	16.78	17.56	14.98	15.76	2.40
		STD DEV	0.012	1.94	0.68	1.49	0.44	0.05	0.44	0.26	0.21	0.30	0.05
		(% STD DEV)	(4.1)	(4.0)	(2.4)	(3.3)	(4.0)	(1.8)	(2.6)	(1.5)	(1.4)	(1.9)	(2.0)

Note: MEAN (6) for Ce and Ce ANOM

Table 11 shows results based on replicate measurements of three rivers: Connecticut, Hudson and Amazon. The excellent precision of the various samples is evident from the data. For the JAN92 Connecticut River samples where 6 replicates were done (5 by ICP-MS), the % Std Dev is generally less than 5, with the exception of Gd and Lu at ~ 8. As explained earlier, calculation of Gd and Lu concentrations after ICP-MS requires significant correction for other interfering REE mass peaks. This could be an explanation for less precise Gd and Lu concentrations in this set of data.

Ten different Sargasso Sea samples were analyzed in duplicate and the results are given in **Table 12**. In addition, one rainwater sample and four samples from a Cape Cod pond were done in duplicate (see **Table 13**). Again, by inspection, the low variability of the replication is apparent. In general, the standard deviation for all of the REEs is less then 5%. This is especially true when the duplicate analyses were both done on the VG 354 TIMS at WHOI. Duplicate agreement is not as good between a TIMS measurement and an ICP-MS measurement of the same sample.

Another way of evaluating the precision of the replicate measurements is to plot the REE concentrations normalized against standard shale values for the REE. The shale-normalized patterns for four measurements of Sargasso Sea water from the BATS program are shown in **Fig. 1**. Both 1 m and 20 m samples from BATS station 44 were analyzed at WHOI and at Harvard (THQ - TIMS). Not only is the precision excellent for the duplicate measurements at each depth, all four measurements can be considered replicates since the surface water at this station is well mixed. **Fig. 2** shows the patterns of four measurements of a Chesapeake Bay composite sample, two run at WHOI and two at Harvard. The precision of the four measurements is evident from the graph.

III. BLANKS

Procedural blanks were processed in several ways. In three blanks (#1, 2 & 3), the enriched isotope spike, along with 50 mg of clean iron carrier, was equilibrated with 50 mL of Ba-Free Milli-Q water. The pH was raised to 8-9 with two-bottle NH_4OH. Although there was an immediate color change associated with the formation of iron (III) hydroxide, the precipitate did not form. The plastic bottles were set aside and observed. It took about one week before the apparently colloidal particles coagulated and settled. The precipitate was then filtered and processed as for actual samples.

Because of this coagulation problem, subsequent blanks (#4, 5, 6, 10, 11 & 12) had 5-10 mL of surface Sargasso seawater added to the Ba-Free Milli-Q, in addition to the carrier and spike, to

TABLE 11

RIVER REPLICATES

REE in pmol/Kg

( ) = % Std. Dev.

MS #	SAMPLE ID	DATE	FILTER	METHOD	Ce ANOM	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
CONNECTICUT RIVER (Sholkovitz, 1992)															
83		JUN91	0.025uM	TIMS-ID-MLA	0.51	38.8	45.6	49.2	10.9	2.0	16.7	11.8	13.1	21.3	3.9
84		JUN91	0.025uM	TIMS-ID-MLA	0.47	42.6	43.8	48.6	11.1	2.1	16.9	12.1	13.4	21.6	3.9
					(5.8)	(6.6)	(2.8)	(0.9)	(1.3)	(2.8)	(0.8)	(1.8)	(1.6)	(1.0)	(1.3)
107		SEP91	0.025uM	TIMS-ID-MLA	0.56	101.0	122.0	112.0	24.4	4.7	29.2	21.4	19.0	27.5	4.8
108		SEP91	refilt.	TIMS-ID-MLA	0.57	95.3	119.0	109.0	23.5	4.6	28.7	21.0	19.1	27.9	4.6
					(1.3)	(4.1)	(1.8)	(1.9)	(2.7)	(1.7)	(1.2)	(1.3)	(0.4)	(1.0)	(3.4)
168		JAN92	0.22uM	ICPMS-ID-SC		NM	93.4	58.6	12.9	2.55	18.0	13.9	16.6	31.1	5.60
169		JAN92	0.22uM	ICPMS-ID-SC		NM	93.9	58.2	12.8	2.54	19.3	13.0	16.8	31.7	5.23
170		JAN92	0.22uM	ICPMS-ID-SC		NM	96.6	56.3	11.9	2.45	16.7	13.0	15.6	30.2	4.95
166		JAN92	0.22uM	ICPMS-ID-MLA	0.91	46.0	95.0	57.7	12.6	2.21	16.0	12.3	16.6	31.3	6.21
167		JAN92	0.22uM	ICPMS-ID-MLA	1.15	31.0	94.6	54.4	12.7	2.42	16.3	13.4	16.0	31.1	5.47
165		JAN92	0.22uM	TIMS-ID-MLA	0.92	49.8	99.4	54.5	12.8	2.47	15.7	12.7	16.3	29.8	5.21
				MEAN (6)			95.5	56.6	12.6	2.44	17.0	13.1	16.3	30.9	5.45
NM = not measurable				STD DEV			2.2	1.9	0.4	0.12	1.4	0.6	0.5	0.7	0.44
				(% STD DEV)			(2.3)	(3.4)	(3.2)	(4.9)	(8.2)	(4.6)	(3.1)	(2.3)	(8.1)
HUDSON RIVER															
Filtered through >5K FILTRON filter															
301		OCT92	>5K	ICPMS-ID-SC			4142	3903	719	132	981	654	390	363	46
309		OCT92	>5K	ICPMS-ID-SC			4071	3901	719	144	1028	642	391	370	48
							(1.2)	(0)	(0)	(6.1)	(3.4)	(1.2)	(0.3)	(1.2)	(3.0)
AMAZON RIVER WATER (Sholkovitz, 1993)															
0.22uM FILTERED															
72		I-1-23B	33.4	TIMS-ID-MLA	0.53	30.0	35.4	35.3	8.8	2.42	14.0	15.1	11.4	9.4	1.26
47		I-1-23A	33.4	TIMS-ID-MLA	0.52	29.8	25.1	36.5	9.9	2.43	14.8	15.0	11.3	9.2	1.25
					(1.3)	(0.5)	(24.1)	(2.4)	(8.3)	(0.3)	(3.9)	(0.5)	(0.6)	(1.5)	(0.6)
44		I-1-14A	33.5	TIMS-ID-MLA	0.38	35.5	29.5	40.8	10.4	2.96	17.4	19.8	14.5	12.6	1.77
71		I-1-14B	33.5	TIMS-ID-MLA	0.38	35.4	30.2	42.4	11.8	2.96	18.3	19.5	15.2	12.6	1.79
					(0)	(0.2)	(1.7)	(2.7)	(8.9)	(0)	(3.6)	(1.1)	(3.3)	(0)	(0.8)

TABLE 12

SEAWATER REPLICATES

REE in pmol/Kg

( ) = % Std. Dev.

MS #	I.D.	DEPTH	METHOD	Ce ANOM	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
SARGASSO SEAWATER (Sholkovitz and Schneider, 1991)														
0.4uM FILTERED														
	20APR89	15M	TIMS-ID-MLA	0.46	15.96	15.66	15.88	3.51	0.92	5.33	5.84	4.74	4.07	0.56
	20APR89	30M	TIMS-ID-MLA	0.46	15.54	15.04	15.64	3.49	0.92	5.12	6.02	4.71	4.07	0.56
				(0)	(1.9)	(2.9)	(1.1)	(0.4)	(0)	(2.8)	(2.1)	(0.4)	(0)	(0)
	14MAY89	20M	TIMS-ID-MLA	0.47	16.58	16.31	16.88	3.73	0.99	5.38	6.09	4.85	4.13	0.57
	14MAY89	40M	TIMS-ID-MLA	0.49	16.22	16.82	17.11	3.60	0.97	5.21	6.02	4.77	4.09	0.56
				(2.9)	(1.6)	(2.2)	(1.0)	(2.5)	(1.4)	(2.3)	(0.8)	(1.2)	(0.7)	(1.3)
SARGASSO SEAWATER (BATS Study)														
0.22uM FILTERED														
53	05APR91	1M	TIMS-ID-MLA	0.55	14.50	13.65	18.17	5.53	0.90	6.54	5.67	4.77	3.93	0.55
92	05APR91	1M	TIMS-ID-MLA	0.37	15.83	12.65	17.53	4.74	0.93	6.31	5.90	4.77	4.10	0.56
				(27.7)	(6.2)	(5.4)	(2.5)	(10.9)	(2.3)	(2.5)	(2.8)	(0.1)	(3.0)	(2.2)
55	05APR91	40M	TIMS-ID-MLA	0.39	15.50	13.02	17.34	4.75	0.94	6.07	5.91	4.77	4.06	0.56
253	05APR91	40M	ICPMS-ID-MLA	0.49	16.22	16.82	17.11	3.60	0.97	5.21	6.02	4.77	4.09	0.71
				(16.1)	(3.2)	(18.0)	(0.9)	(19.5)	(2.2)	(10.8)	(1.3)	(0)	(0.5)	(16.9)
56	05APR91	80M	TIMS-ID-MLA	0.37	15.21	12.15	16.71	4.40	0.93	5.94	5.92	4.76	4.04	0.57
254	05APR91	80M	ICPMS-ID-SC		NM	16.63	17.74	3.63	1.00	6.53	6.00	4.60	4.34	0.77
						(22.0)	(4.2)	(13.6)	(5.3)	(6.7)	(1.0)	(2.4)	(5.2)	(20.9)
57	05APR91	140M	TIMS-ID-MLA	0.39	14.62	12.47	16.59	4.88	0.90	5.85	5.77	4.72	4.01	0.57
255	05APR91	140M	ICPMS-ID-SC		NM	17.97	17.70	4.09	0.76	6.84	5.75	4.67	3.85	0.63
						(25.5)	(4.6)	(12.4)	(11.9)	(11.1)	(0.3)	(0.8)	(2.9)	(6.8)
126	13MAY91	40M	TIMS-ID-MLA	1.17	17.46	25.49	20.37	4.64	1.22	6.50	6.26	4.55	3.90	0.53
314	13MAY91	40M	TIMS-ID-MLA	1.15	17.91	25.75	20.99	5.60	1.20	7.48	6.26	4.73	3.97	0.55
				(1.2)	(1.8)	(0.7)	(2.1)	(13.2)	(1.3)	(9.9)	(0.1)	(2.8)	(1.3)	(3.5)
429	18MAY92	1M	TIMS-ID-MLA	0.44	14.24	13.24	14.99	3.81	0.78	5.39	5.45	4.53	3.89	0.54
454	18MAY92	1M	THQ-TIMS-MLA	0.39	13.65	11.45	14.95	3.75	0.79	5.43	5.52	4.54	3.98	0.54
				(8.3)	(3.0)	(10.3)	(0.2)	(1.1)	(0.8)	(0.5)	(1.0)	(0.2)	(1.6)	(0.2)
430	18MAY92	20M	TIMS-ID-MLA	0.42	13.98	12.47	15.11	3.81	0.82	5.45	5.54	4.68	3.93	0.55
455	18MAY92	20M	THQ-TIMS-MLA	0.38	13.59	11.11	15.05	3.75	0.80	5.48	5.52	4.58	3.98	0.55
				(6.8)	(2.0)	(8.1)	(0.3)	(1.2)	(1.9)	(0.3)	(0.3)	(1.5)	(0.9)	(0.3)
431	18MAY92	40M	TIMS-ID-MLA	0.42	13.91	12.64	15.01	3.77	0.79	5.38	5.47	4.56	3.96	0.55
444	18MAY92	40M	TIMS-ID-MLA	0.52	14.53	15.72	14.66	3.70	0.81	5.31	5.50	4.60	3.96	0.55
				(14.0)	(3.1)	(15.3)	(1.7)	(1.4)	(1.8)	(1.0)	(0.4)	(0.5)	(0.1)	(0)

TABLE 13

MISCELLANEOUS REPLICATES

REE in pmol/Kg

( ) = % Std. Dev.

MS #	I.D.	DEPTH	METHOD	Ce ANOM	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
BERMUDA TUDOR (HILL) TOWER 15 AUG 89 (Sholkovitz, Church, Arimoto, 1993)														
FILTERED ACIDIFIED RAINWATER														
77	BWT		TIMS-ID-MLA	1.24	13.2	25.9	20.0	6.6	0.72	6.94	3.19	1.98	1.53	0.202
93	BWT		TIMS-ID-MLA	1.17	13.6	24.7	20.8	7.6	0.69	7.51	3.16	2.00	1.49	0.221
				(4.1)	(2.3)	(3.3)	(2.6)	(9.6)	(3.0)	(5.6)	(0.7)	(0,7)	(1.9)	(6.4)
GULL POND - WELLFLEET, MA (Johan Schijf; per. comm.)														
0.22uM FILTERED														
273	22JUL92	15M	ICPMS-ID-SC			13.2	10.9	2.83	0.28	4.04	1.19	0.48	1.22	0.256
376	22JUL92	15M	ICPMS-ID-SC			12.1	10.7	3.02	0.30	3.68	1.13	0.63	1.31	0.229
						(6.3)	(1.8)	(4.5)	(6.6)	(6.6)	(3.7)	(18.4)	(5.0)	(7.9)
269	22JUL92	16M	ICPMS-ID-SC			16.7	12.7	3.45			1.30	1.20	1.11	0.269
375	22JUL92	16M	ICPMS-ID-SC			16.0	10.9	3.14			1.49	0.81	1.32	0.257
						(2.8)	(10.3)	(6.5)			(9.8)	(27.0)	(12.4)	(3.2)
271	22JUL92	17M	ICPMS-ID-SC			29.9	14.6	4.34		5.53	1.86		1.62	
374	22JUL92	17M	ICPMS-ID-SC			23.3	14.7	3.95			2.26		1.56	
						(17.5)	(0.2)	(6.7)			(13.7)		(2.6)	
250	19AUG92	17M	TIMS-ID-MLA	1.71	57.8	241.2	84.8	16.5	3.14	16.43				
250	19AUG92	17M	ICPMS-ID-SC			182.6	87.2	14.9	3.69	18.40				
						(19.6)	(1.9)	(7.4)	(11.5)	(8.0)				

FIG 1

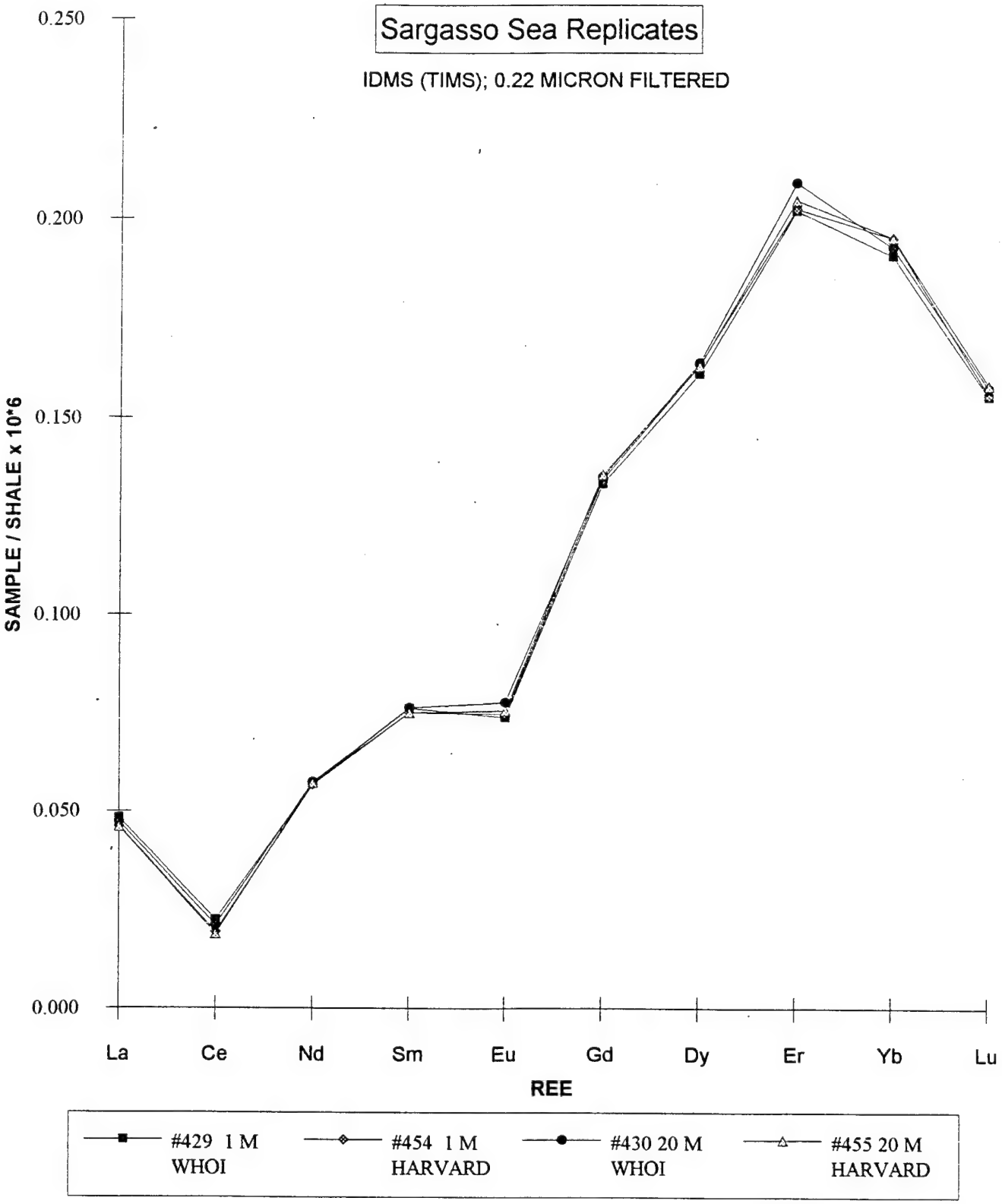
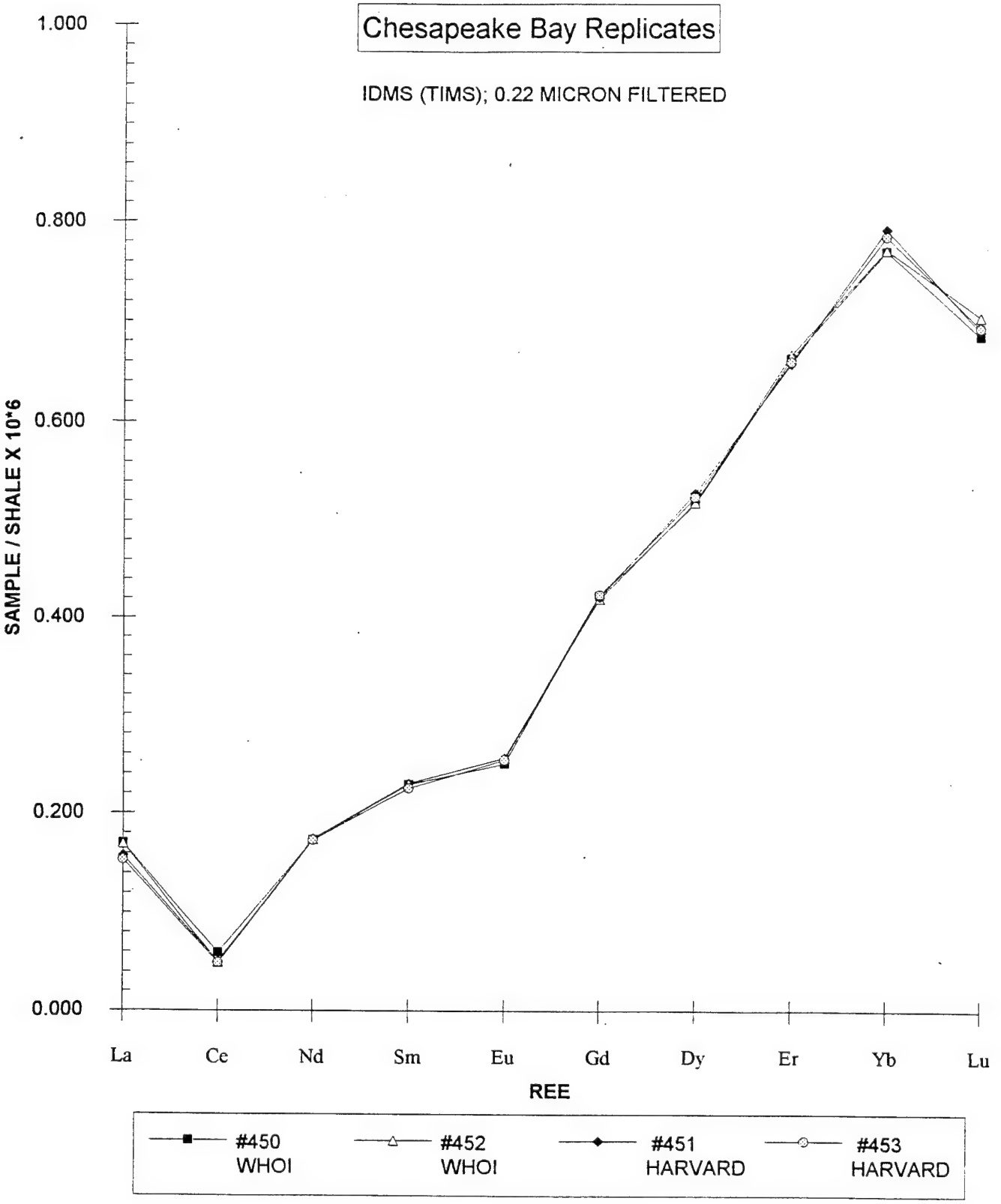

Sargasso Sea Replicates
IDMS (TIMS); 0.22 MICRON FILTERED
SAMPLE / SHALE x 10^6
0.250
0.200
0.150
0.100
0.050
0.000
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu
REE
#429 1 M WHOI
#454 1 M HARVARD
#430 20 M WHOI
#455 20 M HARVARD

FIG 2


Chesapeake Bay Replicates
IDMS (TIMS); 0.22 MICRON FILTERED
1.000
0.800
0.600
0.400
0.200
0.000
SAMPLE / SHALE X 10*6
La
Ce
Nd
Sm
Eu
Gd
Dy
Er
Yb
Lu
REE
#450 WHOI
#452 WHOI
#451 HARVARD
#453 HARVARD

help promote precipitation. In these blanks, the hydroxide precipitation occurred within minutes, as is normal. The REE content of these six blanks were corrected for the seawater contribution.

Three blanks (#13, 14 & 15), composed of only the enriched isotope spike evaporated to dryness, were added directly to the MLA columns. There was no precipitation step or first column.

As can be seen in **Table 14**, only two samples have data for the HREE. Since the measurement of HREE in blanks is difficult to make, the assumption is made that if LREE and MREE are acceptably low, the HREE will be as well.

Based on the average of all measurements, the typical procedural blank contribution to a 1 liter seawater sample is 2-3%. Sm and Gd are exceptions at 5-6%. However, the averages are biased on the high end by #10-12 which had seawater added and were analyzed as a set. As a group, they are significantly higher than the other nine blanks. When these three blanks are eliminated from the computation, the typical blank contribution is 1% or less. Because the error associated with blanks is very small, samples are not corrected for a blank component.

SUMMARY

The method described here allows for the precise determination of the REEs in natural waters at concentrations as low as a few pmol/Kg. The REEs are concentrated from the sample and purified by co-precipitation with iron hydroxide followed by two ion-exchange separations using cation resins. The first mineral acid column separates REE from major and trace elements. The second column, using methyllactic acid, separates the REE into three fractions, eliminating the need for interference corrections during mass spectrometry.

Instrumental analysis is by isotope dilution mass spectrometry (IDMS) using either a VG 354 thermal ionization mass spectrometer or a VG PlasmaQuad inductively coupled plasma-mass spectrometer (ICP-MS). In general, the % Std Dev on all of the REE is 5 or less, based on many duplicate and replicate measurements. The typical procedural blank contribution to a one liter seawater sample is 2-3% or less.

TABLE 14

BLANKS

(pmol)

SAMPLE ID	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
BLK-1	0.180	0.358	0.062	0.006	0.002	0.004	0.268	0.196		0.026
BLK-2	0.044	0.090	0.061	0.031	0.009	0.045	0.058	0.015	0.011	0.001
BLK-3	0.023	0.049	0.008	0.001	0.001					
BLK-4	0.497	0.416	0.201	0.050	0.007	0.018				
BLK-5	0.128	0.254	0.067	0.011		0.008				
BLK-6	0.143	0.278								
BLK-10	0.322	0.725	1.364	0.728	0.009	0.675				
BLK-11	0.460	1.320	1.401	0.731	0.008	0.705				
BLK-12	1.189	0.862	1.441	0.727	0.012	0.666				
BLK-13	0.078	0.091	0.020	0.003						
BLK-14	0.070	0.110	0.011	0.001	0.001					
BLK-15	0.105	0.102	0.014	0.001	0.003	0.001				
AVERAGE	0.270	0.388	0.423	0.208	0.006	0.265	0.163	0.105	0.011	0.014
STD DEV	0.316	0.375	0.602	0.319	0.004	0.323	0.105	0.090		0.013
Seawater (1 L)	16.000	15.700	15.900	3.510	0.920	5.330	5.840	4.740	4.040	0.550
AveBlks/SW (%)	1.7	2.5	2.7	5.9	0.6	5.0	2.8	2.2	0.3	2.5

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APPENDIX A

PROTOCOL FOR REE ANALYSIS OF NATURAL WATERS

I. INITIAL SAMPLE TREATMENT

1. Weigh previously acidified sample plus bottle.

2. Add appropriate amount of spike and weigh again.

3. Add 1.0 mL of "clean" iron carrier solution (~1.0 mg/g).

4. Allow spike and carrier to equilibrate with the sample (at least three days).

5. Precipitate $Fe(OH)_3$ by adding "clean" NH_4OH to the sample bottle. Shake well and let settle.

6. Filter ppt onto acid-cleaned membrane filters (Millipore Co.; Duropore; #GVWP-047-00, (0.22 μm) using an acid-cleaned polycarbonate filter housing (Sartorius, #SM16510/11).

7. Wash the filter housing and filter with Milli-Q water (pH=9) from a squeeze bottle.

8. Disassemble filter unit, remove sample filter and store in a tightly covered plastic filter holder.

9. Save sample bottle. Rinse, dry and take tare weight.

II. CLEAN-UP COLUMN

This column separates major and trace elements from the REE group. The REE are retained on the column while other elements are eluted in the wash fractions.

1. Prepare small quartz columns (columns are stored in ~ 1.0M HCl until use).

2. Weigh 0.3 g. of cation exchange resin (BioRad AG 50W-X8, 100-200 mesh) and transfer to columns with Ba-free Milli-Q water.

3. Wash resin with 4.0 mL of "clean" 4.0M HNO_3, followed by 4.0 mL of "clean" 4.0M HCl.

4. Generate the resin for use with 4.0 mL of "clean" 1.75M HCl.

5. Add 1.0 mL of 1.75M HCl to the sample filter in plastic filter holder. Let precipitate dissolve. Use a plastic pipette tip to manipulate the filter and facilitate dissolution.

6. Transfer sample to column with Eppendorf pipette. Let solution drip through resin.

7. Repeat Steps 5 & 6 two more times.

8. Add a final 0.5 mL of 1.75M HCl to bring the total solution to 3.5 mL

9. Next pass 23 mL of "clean" 1.0M HNO_3 through the column. The purpose of this wash is to remove Ba from the REE fraction.

10. Finally, elute the REE as a group, using 4.0 mL of "clean" 4.0M HNO_3. Collect sample solutions in 5.0 mL conical-bottomed teflon beakers (Savillex Corp, #024T).

11. Evaporate samples to dryness in an air-filtered evaporator box.

III. SEPARATION OF THE REE

A. Column Preparation

1. Prepare large quartz columns (2 mm ID X 35 cm Long).

2. Rinse column with "clean" 2.0M HNO_3. Cap off tip and let column sit with acid until ready to use.

3. Rinse column five times with Ba-free Milli-Q water.

4. Load "clean" resin (BioRad, AG 50W-X4, minus 400 mesh) during the final Milli-Q rinse. An acid-cleaned transfer pipette can be used to load resin. Use ~ 2.0 mL of wet resin.

5. Allow resin to settle by gravity.

6. Remove Milli-Q to neck of column.

7. Add 8 mL of Methyllactic Acid (MLA=0.20M; pH=4.32) and pass through column, under pressure, at 6 psi (N_2 tank).

8. Repeat Step 7 until eluant is no longer acid. Column is ready to use when the eluant is pH=4-5. Check with pH paper.

9. Remove resin with pipette to the 32 cm mark of a previously calibrated column and remove solution to top of neck. Pressure solution to top of resin.

B. Sample Loading

The following steps are summarized in **Table 15**:

1. Add 50 µl of "clean" 0.75M HCl to sample beaker. Allow sample residue to dissolve.

2. Transfer sample to resin with micro-capillary pipette tips (PGC Scientific Co., #71-6310-80). Avoid air bubbles. Pressure solution to top of resin.

3. Add another 50 µl of 0.75M HCl to beaker and transfer to resin. Pressure solution to top of resin.

4. SET DROP COUNTER TO ZERO

5. Add 100 µl of 0.20M MLA (pH=4.32) to resin and pressure to top of resin.

6. Repeat Step 5.

7. Add 0.20M MLA (pH=4.32) to top of column neck with pipette and then add ~2.0 mL more with a graduated cylinder. The resin will shrink below the 32 cm mark due to MLA and pressure.

8. Collect the HREE according to the column calibration scheme. Use 7.0 mL round-bottom teflon beakers.

9. When the HREE have been collected, remove excess solution to top of column neck.

10. Add 7.0 mL of MLA (MLA=0.2M; pH=4.66) to column reservoir and collect the MREE according to calibration scheme.

11. When the MREE have been collected, remove the excess solution to the top of the column neck.

12. Add 5 mL of MLA (MLA=0.35M; pH=4.77) to reservoir and collect LREE.

13. After LREE have been collected, remove and discard used resin and rinse column with "clean" 1.0M HNO_3. Cap off tip and let column sit with acid until next use.

Table 15

Methyllactic Acid Elution Scheme

	Drop Counts		
	Col 4	Col 5	Col 6
50 µl 0.75M HCl	Load Sample		
50 µl 0.75M HCl			
ZERO COUNTER	**0**	..... **0**	**0**
100 µl MLA, pH=4.30			
100 µl MLA, pH=4.30			
200 µl MLA, pH=4.30			
0.20M MLA, pH=4.30 (2.5 mL)			
Collect(HREE)	10-46	10-46	10-46
Change after	46	46	46
0.20M MLA, pH=4.67 (7.5 mL)			
Collect(Gd, Eu, Sm)	47-100	47-100	47-100
Skip	101-134	101-134	101-134
Collect(Nd)	135-186	135-178	135-178
Change after	186	178	178
0.35M MLA, pH=4.77 (5.0 mL)			
Skip(Pr)	187-215	179-202	179-202
Collect(Ce, La)	216-280	203-270	203-270

APPENDIX B

Equipment List for MLA Column

1. Quartz columns - 2 mm ID; 35 cm L	Anderson Glass Co. RFD#1 Old Turnpike Rd. Fitzwilliam, NH 03447
2. Luer tips (PP) - #K420168-0000 Luer frits (PE) - #K420162-0000	Kontes Glass Co. 9000 Spruce St. Vineland, NJ 08360
3. Series 9000 Optical Sensor Model 9100; 1" square opening	Accura Flow Products PO Box 100 Warminster, PA 18974
4. CUB 20000 General Purpose Counter	Red Lion Controls 20 Willow Springs Circle York, PA 17402
5. Power Supply; Model B12G380; 12 VDC	Acopian Corporation PO Box 638 Easton, PA 18042
6. Low Pressure Line Regulator; Model 3702	Matheson Gas Products PO Box 1147 Gloucester, MA 01930
7. Methyllactic Acid (2-Hydroxyisobutyric Acid) #32359-4; 99%; 100 g. bot.	Aldrich Chemical Co. 1001 W. St. Paul Ave. Milwaukee, WI 53233
8. Cation Exchange Resin - AG 50W-X4; minus 400 mesh	Bio-Rad Laboratories 2000 Alfred Nobel Dr. Hercules, CA 94547
9. Microcapillary Pipette Tips (sample loading) #71-6310-80	PGC Scientifics 9161 Industrial Ct. Gaithersburg, MD 20877
10. Teflon Vials 7 mL; rounded bottom; #02.25R 5 mL; conical bottom; #024	Savillex Corporation 6133 Baker Rd. Minnetonka, MN 55345

APPENDIX C

REE Peak Jumping Types for Mass Spectrometry - VG 354

Peak jumping TYPE Number 34 - CeO

Ratio 1 156/158

Intrf 1 156/153 = 4.6777

Channel	Mass	Integration Time (sec)
baseline	159.500	5
1	152.901	5
2	155.900	5
3	157.900	5

Peak jumping TYPE Number 35 - LaO

Ratio 1 155/154

Intrf 1 154/153 = 2.7231

Intrf 2 155/153 = 3.2273

Intrf 3 154/156 = 0.002825

Channel	Mass	Integration Time (sec)
baseline	159.500	5
1	152.901	5
2	153.902	5
2	154.901	5
2	155.901	5

Peak jumping TYPE Number 10 - Eu

Ratio 1 151/153

Channel	Mass	Integration Time (sec)
baseline	155.500	5
1	150.920	5
2	152.921	5

Peak jumping TYPE Number 38 - Sm & NdO

Ratio 1 147/149

Ratio 2 162/161

Channel	Mass	Integration Time (sec)
baseline	140.500	5
1	146.915	5
2	148.917	5
3	160.908	5
4	161.908	5

Peak jumping TYPE Number 14 - GdO

Ratio 1 172/171

Channel	Mass	Integration Time (sec)
baseline	177.500	5
1	170.918	5
2	171.917	5

Peak jumping TYPE Number 18 - Yb

Ratio 1 174/171

Channel	Mass	Integration Time (sec)
baseline	177.500	5
1	170.936	5
2	173.939	5

Peak jumping TYPE Number 23 - Dy & Er

Ratio 1 163/161

Ratio 2 166/167

Channel	Mass	Integration Time (sec)
baseline	157.500	5
1	160.927	5
2	162.929	5
3	165.930	5
4	166.932	5

Peak jumping TYPE Number 26 - Lu

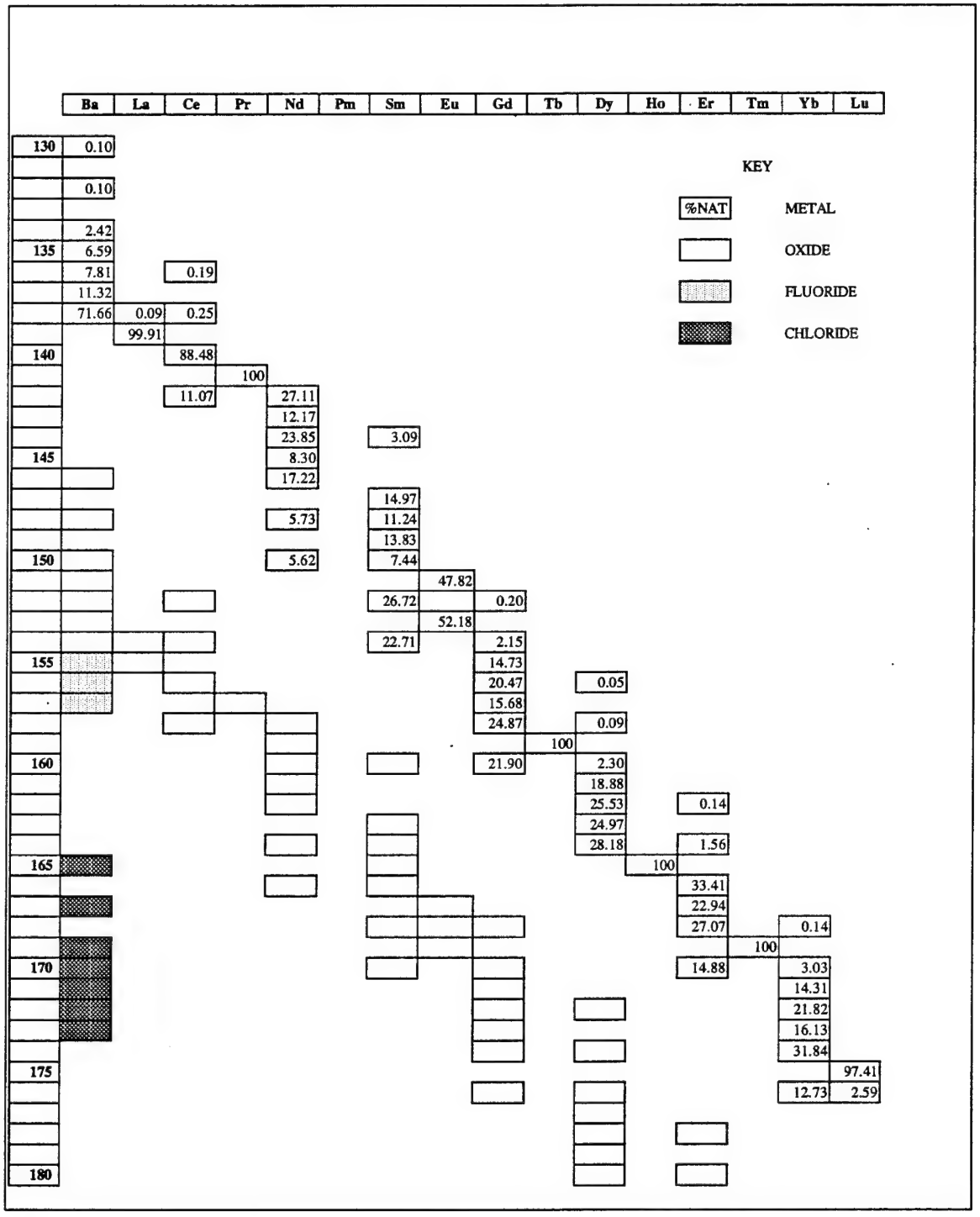
Ratio 1 175/176

Ratio 1 171/176

Channel	Mass	Integration Time (sec)
baseline	177.500	5
1	170.936	5
2	174.941	5
3	175.943	5

APPENDIX D

Ba AND REE MASS COMPOSITIONS



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16. Abstract (Limit: 200 words)

A method is described to measure rare-earth elements (REE) in natural water samples. An iron hydroxide precipitation followed by ion-exchange chromatography is used to concentrate and separate the REE from other matrix components. Additionally, the rare-earth elements themselves are separated into three fractions using an organic acid with a second cation column. Instrumental detection is by isotope dilution mass spectrometry (IDMS) using either thermal ionization mass spectrometry (TIMS) or inductively coupled plasma-mass spectrometry (ICP-MS). Excellent precision is shown by many duplicate and replicate analyses. Blanks are 1-2% or less of samples.

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